# 12.—The cadmium content of some river systems in Western Australia

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*Manuscript received 22 June 1976; accepted 14 September 1976*

Abstract

A stable isotope dilution technique has been used to measure the concentration of cadmium in aqueous solutions with a sensitivity of 0.003 ppb. The concentration of cadmium in the Swan and Peel Inlet river systems in Western Australia has been measured to establish an accurate baseline record against which future measurements can be compared.

The results demonstrate that the cadmium content in the river systems is about one hundredth of the limit set by the World Health Organisation. The data should therefore serve as a basis for comparison with cadmium concentrations in waterways in other parts of the world.

## Introduction

Cadmium is a non-essential, potentially toxic metal that accumulates in human tissue with increasing age. Concern has been expressed at the inadvertent exposure of the general population to this toxic trace element. As is the case with mercury, widespread environmental exposure to cadmium is related to its increased technological use.

A survey of the concentration of cadmium in two river systems in Western Australia has been reported by Rosman and De Laeter (1976) who showed that the levels were about one hundredth of the limit set by the World Health Organisation. (W.H.O. 1963). The present work supplements the above paper and contains a complete description of the analytical results and the experimental procedure, and additional results relating to the reservoir systems and the sediment in the Peel Inlet.

Unfortunately there is still a paucity of accurate information on the content of cadmium in natural waterways, particularly in regions where there is an absence of industrial activity giving atmospheric contamination. Doolan and Smythe (1973) have recently measured the cadmium content in a number of waterways in eastern Aust alia. The present study complements this investigation for waterways in Western Australia. The stable isotope dilution technique used in this project is sufficiently sensitive to explore the variations in cadmium content along the waterways.

## Experimental procedure

The loss of trace amounts of metallic ions on container walls during sample collection, handling and storage of aqueous solutions has been recognised for some time. Struempler (1973) showed that polyethylene containers did not adsorb cadmium from aqueous solutions, could be readily cleaned, and exhibited a very low cadmium blank. Consequently the 500 ml containers used in this project were made from high density polyethylene, and the chemical processing was carried out as soon as possible after the samples were collected.

The polyethylene bottles were cleaned with high purity 6M HCl for several weeks before sample collection. At the collection point each bottle was flushed several times with the river water before the sample was taken.

A 200 g aliquot of each water sample was acidified to a final concentration of 1M with HCl in a flask which had already been spiked with an isotopically enriched $^{111}$Cd tracer. After ensuring that the spike and sample were well mixed, the solution was placed on a large silica column containing $\sim$ 2 g of Dowex AG1 x 8 (100-200 mesh), anion exchange resin which had previously been equilibrated with 1M HCl. After washing the column with several column volumes of 1M HCl, the cadmium was eluted with 4 column volumes of 1M $HNO_3$ and collected in a teflon beaker. The eluate was taken to dryness, the residue was redissolved in a minimum of 0.1M HCl and transferred to a small ion exchange column containing $\sim$ 1 g of Dowex AG50 x 8 (100-200 mesh) cation exchange resin, equilibrated at 0.1M HCl. The Cd was eluted with 6 column volumes of 0.5M HCl and after taking to dryness, was ready for mass spectrometric analysis.

The stable isotope dilution technique has a number of advantages when compared with many other analytical techniques. Because of its excellent sensitivity, high accuracy and precision, it is ideally suited to the analysis of cadmium in the environment. Doolan and Smythe (1973) have drawn attention to the necessity of developing more sensitive and accurate methods of analysing cadmium in the range 2 x $10^{-2}$ to 10 ppb (gram metal per $10^9$ gram water). The isotope dilution technique enables this to be achieved provided the blank is small and accurately known.

A blank was included with each batch of samples undergoing chemical processing. The blank was observed to vary over the period the analyses were made, but was found to be about 1.8 ng. The 6M HCl which was used to acidify the samples and prepare other solutions needed for the extraction was the main source of this cadmium.

The samples were analysed in a 30.5 cm radius, 90° magnetic sector field solid source mass spectrometer equipped with an electron

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Figure 1.—Sample locations for the Swan River system.

multiplier. The samples were mounted on a single rhenium filament using the silica gel loading technique (Cameron *et al.* 1969). Full details of the mass spectrometric procedures used in the project are given by Rosman and De Laeter (1975).

### Results and discussion

Two river systems were selected for study. The Swan River and its tributaries is the major river system for Perth and the surrounding metropolitan area (Figure 1). The second system studied is south of Perth near the Peel Inlet (Figure 2).

The first set of samples was collected during the period 26 April to 24 May 1975. There was little rain in the 6 months preceding sample collection or during the sample collection period itself. The second set of samples was collected from 26 February to 11 April 1976 when conditions similar to those in the 1975 collection period prevailed. Wherever possible the samples were collected from the centre of the smaller streams or away from the bank at places where the river was wide.

#### *Swan River system*

The information on the Swan River system is given in Table 1 and includes sample number, collection date, locality and cadmium concentra-

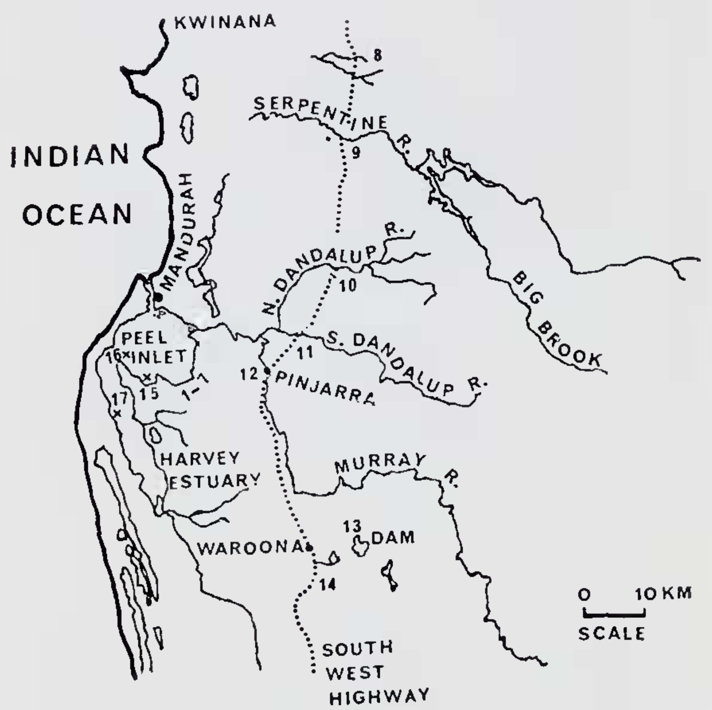


Figure 2.—Sample locations for the Peel Inlet river system.

tion. The corresponding sample numbers and localities are shown in Figure 1. The cadmium concentration listed with each location is the mean of duplicate analyses, and the error for each sample is listed in the table. The greater part of the error is due to the uncertainty in correcting for the chemistry blank.

**Table 1**

*Cadmium content of the Swan River System*

| Sample no. | Collection date | Locality | Concentration (ppb) |
|---|---|---|---|
| | | *Lower Swan* | |
| 1 | 26 April 1975 | Fremantle Bridge | 0.064 ± 0.003 |
| 2 | 26 April 1975 | Crawley | 0.14 ± 0.01 |
| 3 | 26 April 1975 | Kings Park Foreshore | 0.070 ± 0.003 |
| 4 | 26 April 1975 | Narrows Bridge | 0.10 ± 0.05 |
| 5 | 26 April 1975 | Causeway (South) | 0.12 ± 0.01 |
| 6 | 17 May 1975 | Causeway (North) | 0.21 ± 0.02 |
| 7 | 17 May 1975 | Rivervale | 0.44 ± 0.01 |
| 8 | 17 May 1975 | Garratt Road Bridge | 0.14 ± 0.01 |
| 9 | 17 May 1975 | Ashfield | 0.068 ± 0.006 |
| 10 | 17 May 1975 | Guildford | 0.10 ± 0.06 |
| 11 | 26 April 1975 | Bassendean Bridge | 0.04 ± 0.01 |
| | | *Middle Swan* | |
| 12 | 26 April 1975 | Caversham Bridge | 0.17 ± 0.007 |
| 13 | 11 May 1975 | Midland Junction | 0.082 ± 0.003 |
| 14 | 11 May 1975 | Junction of Jane Brook | 0.061 ± 0.003 |
| 15 | 10 May 1975 | Off Swan, on Suzzana Brook Tributary | 0.02 ± 0.01 |
| 16 | 11 May 1975 | Gnangara Road (near Church) | 0.14 ± 0.01 |
| 17 | 10 May 1975 | Baskerville | 0.13 ± 0.01 |
| | | *Upper Swan— Avon River* | |
| 18 | 10 May 1975 | Walyunga National Park | 0.14 ± 0.01 |
| 19 | 10 May 1975 | Walyunga National Park (up stream) | 0.010 ± 0.006 |
| 20 | 24 May 1975 | West Toodyay | 0.063 ± 0.003 |
| 21 | 24 May 1975 | Toodyay—Northam | 0.013 ± 0.003 |
| 22 | 24 May 1975 | York | 0.010 ± 0.003 |
| 23 | 24 May 1975 | Gilgering | 0.04 ± 0.01 |
| 24 | 24 May 1975 | East Kokeby Bridge | 0.06 ± 0.02 |
| | | *Helena River* | |
| 25 | 26 April 1975 | Near Junction with the Swan River | 0.04 ± 0.01 |
| 26 | 26 April 1975 | Guildford | 0.04 ± 0.01 |
| 27 | 26 April 1975 | Guildford | 0.02 ± 0.01 |
| 28 | 26 April 1975 | Bellevue | 0.03 ± 0.01 |
| 29 | 26 April 1975 | Bellevue | 0.014 ± 0.005 |
| 30 | 26 April 1975 | Boya | 0.010 ± 0.003 |
| 31 | 26 April 1975 | Darlington | 0.006 ± 0.003 |
| 32 | 7 March 1976 | Mundaring Weir | 0.04 ± 0.01 |
| | | *Canning River* | |
| 33 | 20 May 1975 | Canning Bridge | 0.07 ± 0.03 |
| 34 | 20 May 1975 | Mt. Pleasant | 0.06 ± 0.01 |
| 35 | 20 May 1975 | Rossmoyne | 0.032 ± 0.006 |
| 36 | 20 May 1975 | Riverton | 0.071 ± 0.006 |
| 37 | 20 May 1975 | Riverton Bridge | 0.06 ± 0.03 |
| 38 | 20 May 1975 | Nicholson Road Bridge (Canning-ton) | 0.024 ± 0.003 |
| 39 | 20 May 1975 | Thornlie | 0.035 ± 0.003 |
| 40 | 8 March 1976 | Canning Reservoir (Nr Dam Wall) | 2.2 ± 0.1 |
| 41 | 25 March 1976 | Canning Reservoir (Nr Dam wall) | 1.4 ± 0.1 |
| 42 | 25 March 1976 | Canning Reservoir (upstream) | 0.30 ± 0.01 |
| 43 | 8 March 1976 | Tap water, Ross-moyne | 0.020 ± 0.003 |
| 44 | 26 February 1976 | Tap water, Bentley | 0.030 ± 0.003 |
| 45 | 24 March 1976 | Tap water, Kala-munda | 0.020 ± 0.003 |
| 46 | 10 April 1976 | Tap water, Roley-stone | 0.070 ± 0.004 |
| 47 | 16 March 1976 | Bore water, Perth area | 0.005 ± 0.003 |

As can be seen in Table 1 the data on the Swan River system has been subdivided into regions. In the Lower Swan the cadmium concentrations are about 0.1 ppb except upstream from the Causeway where a value of 0.44 ppb was obtained. This is presumably related to the higher than average level of industrial activity in the area. It is apparent however that the quantity of cadmium is sufficiently small to be quickly diluted, so that a few km downstream it had decreased to 0.21 ppb and then to 0.12ppb. Bowen (1966) states that the cadmium concentration in normal sea water is 0.11 ppb, and our measurements at sample collection points 1-4 are in good agreement with this value. The Middle Swan portion of the river is situated amongst vineyards in a semi-rural area. The cadmium concentration is again of the order of 0.1 ppb in this region.

The course of the Swan River now changes as it traverses the Darling Scarp. To the east of the Darling Scarp for some 60 km, are State Forests and farmlands. The Swan River traverses the Walyunga National Park, which is just to the east of the Darling Scarp. It is interesting to note that the cadmium content of the water collected near the picnic area in the park (Sample 18) was 0.14 ppb, whereas a few km upstream the cadmium content decreased by a factor of 10. This could be the result of contamination at the picnic site, or alternatively be associated with the rocks underlying this region of the river. A large basic intrusion cuts across the river in the vicinity of the sample collection site, whereas most of the surrounding area consists of granite rocks. Rosman and De Laeter (1974) have shown that granitic rocks have substantially smaller cadmium concentrations than basic rocks, and it is therefore possible that the high cadmium content in sample 18 is an indicator of the underlying rock type It is unlikely that the effect would have been measurable at periods of the year when the river is flowing rapidly. The lower concentration level is maintained in the Avon River as it flows through Toodyay and Northam, and does not increase to any great extent in the upper reaches of the Avon River at York and Beverley, even though the river at the time of sample collection consisted of a series of stagnant pools south of Northam.

The cadmium concentrations are extremely low throughout the length of the Helena River region despite the fact that the river is situated along the Darling Scarp in a semi-residential area. Sample 31 came from a forested catchment area. The water was clear and fast moving and gave the lowest cadmium value of all the samples of 0.006 ppb. A sample of water from Mundaring Weir gave a higher value of 0.04 ppb.

The Canning River is tidal for most of the localities where samples were collected. The average of the cadmium concentrations over this region is 0.06 ppb, but further up-stream where it is no longer tidal, the mean concentration is half this value.

Three water samples were collected from the Canning Reservoir in March 1976. Two of the samples were collected near the retaining wall of the reservoir, one from the east bank and the other from the west bank. Both gave surprisingly high Cd concentrations of 1.4 and 2.2 ppb respectively. Another sample, collected approximately 2 km upstream near the west bank, gave a value of 0.3 ppb. Water samples from taps in the metropolitan area gave values between 0.02 to 0.07 ppb, and typical river water values as measured in this study are of the order of 0.05 ppb. Thus one would have expected the Cd concentration of water in the Canning Reservoir to be approximately 0.05 ppb, yet the measured values are significantly higher.

The Canning Reservoir samples were collected in March 1976, at the end of a long dry summer, during which little influx of water took place from the catchment area. The water in the reservoir was quite low, and the samples were collected from close to the surface. It appears that during the hot summer period the water in the Canning Reservoir collects into stratified layers, between which little mixing takes place. The topmost layer loses water through evaporation, and hence the concentration of dissolved elements in this surface layer would increase as the summer progresses. It is possible that fallout of atmospheric particulates also contributes to the cadmium content of this upper water layer. It is also possible that the catchment water into the Canning Reservoir has a higher cadmium content than the Mundaring Reservoir where most of the water percolates through adjacent sediments. The first influx of fresh, catchment-area water into the Canning Reservoir in winter would cause the stratified layers to mix, and a much lower cadmium concentration would be expected throughout the reservoir. The metropolitan area receives water from a number of sources, the Canning Reservoir being one of them. In some areas this water is supplemented by water from artesian and subartesian bores. This bore water has an extremely low cadmium concentration (<0.01 ppb), and this will have the effect of lowering the cadmium concentration in tap water. In addition water is drawn off the Canning Reservoir from a series of outlet pipes situated at different levels below the surface, and the resultant mixture is then reticulated to the metropolitan area.

### *Peel Inlet system*

Peel Inlet is situated some 50 km south of Perth and is a large body of salt water connected to the sea by a narrow channel. The surrounding area is mainly rural, although in the close vicinity of the Peel Inlet there is a residential area. The Murray River and its tributaries flow into the Peel Inlet. The data for this system are given in Table 2, and the sample locations shown in Figure 2.

The cadmium concentrations in the Peel Inlet are remarkably uniform, and the average value for the inlet as a whole is about 0.04 ppb. It is possible that over the summer months when there is little interchange of water with the ocean, the cadmium content of the water is reduced by adsorption into the underlying sediments of the Peel Inlet. Gardiner (1974) has shown that cadmium is adsorbed on river muds, and that adsorption and desorption processes are likely to be major factors in controlling the concentration of cadmium in natural waters. It is likely that in the future, pollution will increase in the Peel River system. It would therefore be desirable to monitor the cadmium content of the inlet and compare it with the 1975 base values. In April 1976 another three water samples were collected from the Peel and Harvey Inlets. These additional samples gave cadmium concentrations of 0.06, 0.07 and 0.11 ppb. The first two samples are only slightly higher than the average value of 0.04 ppb measured in the previous year.

**Table 2**

*Cadmium content of the Peel Inlet river system*

| Sample no. | Collection date | Locality | Concentration (ppb) |
|---|---|---|---|
| 1 | 9 May 1975 | *Peel Inlet* | 0.051 ± 0.003 |
| 2 | 9 May 1975 | *Peel Inlet* | 0.046 ± 0.006 |
| 3 | 9 May 1975 | *Peel Inlet* | 0.050 ± 0.006 |
| 4 | 9 May 1975 | *Peel Inlet* | 0.040 ± 0.003 |
| 5 | 9 May 1975 | *Peel Inlet* | 0.041 ± 0.003 |
| 6 | 9 May 1975 | *Peel Inlet* | 0.020 ± 0.005 |
| 7 | 9 May 1975 | *Peel Inlet* | 0.051 ± 0.008 |
| | | *South Western Highway river crossings* | |
| 8 | 15 May 1975 | Mundijong (Medulla Brook) | 0.010 ± 0.006 |
| 9 | 15 May 1975 | Serpentine (Serpentine River) | 0.031 ± 0.006 |
| 10 | 15 May 1975 | North Dandalup (Nth Dandalup River) | 0.142 ± 0.007 |
| 11 | 15 May 1975 | South Dandalup (Sth Dandalup River) | 0.101 ± 0.005 |
| 12 | 15 May 1975 | Pinjarra (Murray River) | 0.022 ± 0.004 |
| 13 | 15 May 1975 | Waroona Dam .... .... | 0.023 ± 0.004 |
| 14 | 15 May 1975 | Hamel (Irrigation Channel) | 0.151 ± 0.005 |
| | | *Peel and Harvey Inlets* | |
| 15 (a) | 12 April 1976 | Robert Bay, Peel Inlet | 0.060 ± 0.005 |
| 15 (b) | 12 April 1976 | Core Sample (Top) .... | 253 ± 12 |
| 15 (c) | 12 April 1976 | Core Sample (Bottom) | 74 ± 4 |
| 16 (a) | 12 April 1976 | Near Channel, Peel Inlet | 0.110 ± 0.007 |
| 16 (b) | 12 April 1976 | Core Sample (Top) .... | 8 ± 1 |
| 16 (c) | 12 April 1976 | Core Sample (Bottom) .... | 35 ± 3 |
| 17 (a) | 12 April 1976 | Harvey Inlet, West Bank | 0.070 ± 0.005 |
| 17 (b) | 12 April 1976 | Core Sample (Top) .... | 49 ± 3 |
| 17 (c) | 12 April 1976 | Core Sample (Bottom) | 222 ± 11 |

To test the hypothesis that much of the cadmium is adsorbed on underlying sediments, core samples from the three additional locations were also collected. The core samples were approximately 10 cm long, and 0.5 g portions from the top and bottom of the cores were digested by a $HF$-$HClO_4$ mixture, and then subjected to an extraction procedure described by Rosman and De Laeter (1974). The results are listed in Table 2. At first sight the data may appear confusing, but the type of material sampled is significant. The Robert Bay core sample was very rich in humic constituents at the surface, whereas the bottom portion contained a higher portion of clay and other silicates. The Harvey Inlet sample was almost the reverse of the Robert Bay sample, the bottom part of the core being richer in humic material, whereas the upper portion contained some small shells. The core sample from the channel comprised white sandy material throughout its length, and the low cadmium concentration reflected this preponderance of silicate material.

Thus the underlying river mud acts as a sink for the dissolved cadmium, most of the cadmium being adsorbed in regions where humic material predominates. This conclusion is in agreement with the work of Gardiner (1974), who found that the humic constituents of mud are principally responsible for its adsorptive properties. Gardiner has shown that in any fresh water system which has attained equilibrium, the concentration of cadmium on finely divided solids may be 5 000-50 000 times higher than in solution. In the present case the factor is at the lower level of this range, but it must be remembered that the water is salty and the inlet is open to the sea for much of the year.

Florence and Batley (1976) have shown that a proportion of the cadmium in sea water is present either as organic chelates or adsorbed on organic or inorganic particles. Colloidal particles are not retained by most ion-exchange resins because the resin pore size is too small to allow the colloids to enter the resin network (Samuelson 1963). It was therefore decided to check if the chemical extraction used in this project was effective in measuring the total cadmium content in the water samples. A sample of water was taken from the upper reaches of the Helena River for this purpose and four 100 ml aliquots from the same polyethylene bottle were analysed.

The first was spiked with $^{111}Cd$ and evaporated to dryness with distilled $HNO_3$. 6M HCl was added to the residue and then taken to dryness. The residue was treated with 1M HCl and subjected to the normal ion exchange procedure. A Cd concentration of $0.01 \pm 0.01$ ppb was obtained. The second and third samples were spiked and allowed to equilibrate for 3 and 7 days respectively, before processing. The last sample taken was observed to contain some particulate matter. This sample was spiked and allowed the normal mixing time. The second, third and fourth determinations yielded concentrations of $0.01 \pm 0.01$, $0.01 \pm 0.01$ and $0.02 \pm 0.01$ ppb respectively. The first three samples gave identical concentrations whereas the higher value obtained for the fourth sample is attributed to the presence of particulate matter.

The remaining 7 samples were collected at river crossings between Mundijong and Waroona along the South West Highway. This highway skirts the base of the Darling Scarp and is crossed by some 14 streams and rivers within the 60 km sector sampled. The water samples were collected upstream from the highway and as near to the centre of the stream as possible. After leaving the Darling Scarp the waterways traverse the coastal plain, and many finally feed into Peel Inlet. The waterways originate in the ranges behind the Darling Scarp in a region of virgin bush. The Serpentine and Waroona reservoirs are situated on two of the major streams. The cadmium concentrations are very low, for the most part being less than 0.1 ppb.

## Conclusions

The World Health Organisation has declared that the maximum advisable concentration limit for cadmium in drinking water is 10 ppb (W.H.O. 1963). The recommended maximum level for irrigation purposes is 5 ppb for continuous use (Committee on Water Quality Criteria 1968). The results of this study demonstrate that the cadmium content in the two major river systems in south Western Australia are of the order of 100 times lower than the W.H.O. limits. The data indicate that the cadmium content tends to decrease upstream from the mouth of the rivers studied, and that in the reservoir catchment areas the cadmium content is as low as 0.01 ppb in many places.

These values compare very favourably with waterways in other parts of the world. Abdullah and Royle (1972) give a value of 0.41 ppb for "clean" stream water in Wales, whilst in some of the rivers in England the average cadmium content is approximately 25 ppb (Valdez 1975). In North America many streams contain more than 1 ppb cadmium (U.S.G.S. 1970).

Dale *et al.* (1974) have measured the cadmium content of a number of rivers in Victoria, Australia. Unfortunately their detection limit was 30 ppb and the cadmium content of many of the samples was below their detection limit. However the cadmium content of a number of samples was in excess of 30 ppb. Doolan and Smythe (1973) also found a range of cadmium concentrations (from $< 0.02$ to 7.7 ppb) in some rivers in New South Wales, Australia. The sensitivity of their technique was 0.02 ppb which compares favourably with ours.

It is likely that much of the published work on the cadmium content in water has been based on analytical techniques which were incapable of measuring accurately below the ppb level. The present study has succeeded in adapting the stable isotope dilution technique using solid source mass spectrometry to the measurement of cadmium in river waters, and we believe the measured concentrations establish a definitive set of low level base line determinations for cadmium in the environment.

*Acknowledgements.*—The authors would like to thank the following graduate students who contributed to the project: I. D. Abercrombie, G. L. Cody, L. P. Costa, H. K. Cowan, C. B. McKay, D. R. Mills, M. T. Prosser, D. A. Ryan, S. Sandri, R. C. Seinor and D. B. Thornton.

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